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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of	)	
	)	
R. Terry K. Baker et al.	)	Art Unit 1754
	)	
Serial No. 10/015,353	)	Before the Examiner
	)	
Filed: December 11, 2001	)	Stuart L. Hendrickson
	)	

**Preparation of Multifaceted Graphite  
Nanotubes**

Honorable Assistant Commissioner of Patents and Trademarks  
Washington, D. C. 20231

**DECLARATION UNDER 35 CFR 1.132**

R. Terry K. Baker declares and says:

**That** he is a named inventor on the instant application.

**That** he has read and understands the arguments presented by the examiner in the Office  
Action dated December 10, 2003.

**That**he has read and understands US Patent No. 6,143,6890 to Moy that was cited  
against insant claims 8, 9, 10, 13, and 14.

**That**he disagrees with the Examiner's position that an imperfection in the Moy  
cylindrical fibrils can result in mutifaceted nanotubes.

**That**he also disagrees with the Examiner's position that the use of hydrogen and carbon  
monoxide would be an obvious expedient for Moy which teaches only the use of carbon  
monoxide without hydrogen.

**That**he has had the following experiments performed, under his direction, to show that  
hydrogen is a critical part of the instantly claimed process and that only Ni and Co, and  
not Fe will produce multifaceted nanotubes.

**Experiments Performed Under the Direction of R. Terry, K. Baker**

The catalysts used in these experiments were prepared according to identical procedures by mixing either Fe, Ni or Co with MgO in a ratio of 0.6:1 and then these mixtures were initially calcined at 500°C and reduced in H<sub>2</sub> at 600°C. Following this step, each catalyst system was reacted in either pure CO or various CO/H<sub>2</sub> mixtures at 600°C for a period of 5 hours in a horizontal flow reactor unit.

At the termination of a given experiment, the solid carbon product was removed from the reactor and the yield of the deposited material was determined by weight difference of the catalyst before and after reaction. A section of each sample was then ultrasonically dispersed in iso-butanol and a drop of the resulting suspension was applied to a holey carbon support grid. These samples were examined in a JEOL 2000EXII high-resolution TEM (lattice resolution 0.18 nm). The data presented below were obtained from a number of areas of a given specimen and represent the typical observed appearance of the solid carbon product(s) from each experiment.

**Examination of (a) Fe/MgO-CO and (b) Fe/MgO-CO/H<sub>2</sub> (where the ratio of CO:H<sub>2</sub> was systematically varied from 9:1 to 1:4).**

**(a) Fe/MgO-CO**

When this sample was examined no evidence for the formation of any type of nanofibrous material was observed. The entire carbonaceous deposit consisted of graphitic shells (average width 200 nm) that had grown and eventually encapsulated the iron particles. These types of deposits are frequently referred to as "onion-like" structures in the literature and an example is shown schematically in the figures that are an Addendum hereto.

**(b) Fe/MgO-CO/H<sub>2</sub>**

The behavior of these catalyst systems was quite different to that described above, demonstrating the impact of H<sub>2</sub> on the reaction. All specimens showed the existence of carbon nanofibers, the only difference from each sample being the respective yields as a function of the CO/H<sub>2</sub> ratio. Examination of the nanofibrous deposits at high-resolution showed that they consisted of graphite sheets that were aligned in a direction

perpendicular to the fiber axis in a so-called "platelet" arrangement (average width 104 nm). A schematic representation of these structures is given Addendum thereto. No evidence for the formation of either vermicular shaped or multi-walled faceted carbon nanotubes was found in any regions of these many specimens.

Examination of (c) Co/MgO-CO and (d) Co/MgO-CO/H<sub>2</sub> (where the ratio of CO:H<sub>2</sub> was systematically varied from 39:1 to 1:4).

**(c) Co/MgO-CO**

Examination of the solid carbon product from this system indicated that the deposit consisted exclusively of nanofibrous structures; no evidence for the formation of other types of carbon being found. At high-resolution it was apparent that the fibrous material was comprised of graphite sheets that were aligned in a direction parallel to the growth axis giving the material a tubular appearance (average width 25 nm). From observations of features where the ends of the nanotubes were tilted normal to the electron beam it was possible to ascertain the existence of hexagonal-shaped cross-sectional features, indicating the multi-faceted nature of the nanotubes. A schematic rendition of the multi-walled faceted carbon nanotubes is presented in the Addendum hereto.

**(d) Co/MgO-CO/H<sub>2</sub>**

Many samples from experiments where the Co/MgO powder were reacted in various compositions of CO/H<sub>2</sub> were examined. While there were variations in the yields of solid carbon, no other differences in the composition of the deposits was evident. In all cases, nanofibrous carbon structures were the only type of material present. High-resolution TEM examination confirmed that the structural characteristics were identical to those produced from the same catalyst treated in pure CO, that is the fibers were in the form of multi-walled faceted carbon nanotubes. The presence of H<sub>2</sub> in the reactant mixture was found, however, to exert a significant impact on the average width of the nanotubes, which were on average 8.6 nm in width for CO/H<sub>2</sub> mixtures in the ratio (19:1 to 4:1).

Examination of (e) Ni/MgO-CO and (b) Ni/MgO-CO/H<sub>2</sub> (where the ratio of CO:H<sub>2</sub> was systematically varied from 9:1 to 1:4).

(e) Ni/MgO-CO

When this catalyst system was treated in pure CO, gravimetric measurements indicated that virtually no catalyzed growth of solid carbon took place at 600°C.

(f) Ni/MgO-CO/H<sub>2</sub>

While the amount of solid carbon product was the lowest of the three iron transition metals, it was significant that the material was found to, consist entirely of nanofibrous structures. When examined at high-resolution the structural features of the fibers were identical to those generated from the corresponding Co/MgO systems, i.e. they were multi-walled faceted carbon nanotubes. On average these fibers were about 14 nm in width, being substantial larger than those produced under the same conditions from the Co/MgO catalyst system.

I hereby declare that all statements made herein are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Date 2/11/04

  
R. Terry K. Baker